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Study of spin coated organic thin film under spectrophotometer

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Abstract : Thin films of organic compound Calix resorcinarene are deposited by spin coating method at different spinning speed and different concentrations. Films are studied under UV double beam spectrophotometer. Film thickness data are estimated from absorption spectra which peaks around 454 nm. Peak absorbances are found to be in consistent with spinning speed and solution concentration. The relation between film thickness h and spin speed ω obey power law relation of the form $h \propto \omega^{-1/2}$. This is in agreement with the theoretical model of spin coating mechanism. Increasing solution concentration results in thicker film. This is presumably because of increased fluid viscosity.

Keywords : UV absorption spectrophotometer, spin coating, Newtonian fluid, non-Newtonian fluid.

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1. Introduction

In addition to the inorganic materials (silicon chips) for microelectronic and optoelectronic applications, attention has also been focussed on the organic counterpart in the form of thin films. Among different techniques for organic thin film deposition, spin-coating method has the merit of conveniences, use of low cost equipment and fast operating. Spin coating is general a convenient and reproducible method for applying highly uniform thin films to substrates of all kinds. It has applications in various industries, including the use of polymeric photo resist for photolithography [1] Sol–gel films for dielectric applications [2,3] planner structure for various optical applications [4] and microelectronic industries for fabrication of integrated circuits. This paper deals with the experimental estimation of the thickness of the spin coated Calix [4] resorcinarene film by spectrophotometric technique and claims to verify the relationship between the film thickness and spin speed. Among different optical probes for characterisation of thin films, spectrophotometry seems to be highly challenging one. With this instrument absorbance at various wavelength can be determined. With the brief review of the mathematical modeling of the spin coating method, this paper describes the experimental details of the coating mechanism and estimation of film thickness from absorption spectra.

2. Mathematical modeling of spin coating

The first mathematical model of the spin coating process was given by [5] for a Newtonian fluid. The fluid assumed to be rotating in an infinite plane. Coriolis force and gravitational gradient were neglected.

Using cylindrical polar co-ordinates (r, θ, z) with origin at the center of rotation, z perpendicular to the plane, and the axes r and θ rotating with the plane with angular velocity ω, the balance between viscous and centrifugal forces per unit volume for Newtonian fluid is given by

$$-\eta \left(\frac{d^2v}{dz^2}\right) = \rho\omega^2 r, \qquad (1)$$

where η = viscosity, ρ = fluid density and v = velocity in the direction r.

Integrating twice with respect to z and putting boundary condition that at the free surface of the fluid the shear is zero *i.e.*

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$\frac{dv}{dz} = 0$ at $z = h$ we get

$$V = \frac{1}{\eta}(- \tfrac{1}{2} \rho\omega^2 rz^2 + \rho\omega^2 rhz^2).$$

The radial flow q per unit length of the circumference is given by

$$q = \int_0^h v(z)dz = \left(\rho\omega^2 rh^3\right)/3\eta . \quad (2)$$

The eq. for continuity is given by

$$\frac{\partial h}{\partial t} = \frac{\partial(rq)}{\partial r} \quad (3)$$

Use of equation (2) in (3) yields

$$\frac{\partial h}{\partial t} = \frac{1}{r}\frac{\partial(r^2h^3)}{\partial r}$$

where $K = \rho\omega^2/3\eta$. (4)

Before seeking general solution of eq. (4) let us consider the special solution, which depends only on time t, if the distribution of solution is uniform at the beginning, from eq. (4) we can get

$$dh/dt = -2Kh^3 . \quad (5)$$

Integration both sides with proper limits *i.e.* at $t = 0$, $h = h_0$ and at t, $h = h_t$, we get

$$h_t = h_0/\left(1+4h_0^2Kt\right)^{1/2} = h_0/\left[1+4h_0^2\rho\omega^2 t/3\eta\right]^{1/2} . \quad (6)$$

Meyerhofer [6] developed a spin model using the equation of continuity for a Newtonian fluid but allowed to the solvent to evaporate during spinning process. He approximated that the height of the fluid h could be separated into the height of the solid S and the height of the solvent L *i.e* $h = S + L$.

By expressing the concentration of the solid $C(t)$ to be $C(t) = S/(S + L)$, one can obtain from the equation of continuity

$$\frac{dS}{dt} = - C(t)\frac{2\omega^2h^3}{3\vartheta} \quad (7)$$

where ϑ is the kinetic viscosity $\left| = \frac{\eta}{\ } \right|$. Including the liquid evaporation rate ϕ, the change in liquid height can be expressed as

$$\frac{dL}{dt} = -[1 - C(t)]\frac{2\omega^2h^3}{3\vartheta} - \phi . \quad (8)$$

the viscosities of these solutions has been reported to be the power law function of the concentration which can be written as

$$\vartheta = \vartheta_L + \vartheta_S\, C^{\gamma}(t), \quad (9)$$

where ϑ_L and ϑ_S are the viscosities of solvent and solid respectively and $\gamma = 2.5$. The final film height can be simplified to the form

$$h = \left[\frac{3C^3(t)\vartheta_0\phi}{2\{1-C_0(t)\}\omega^2}\right]^{1/3}$$

or $h \propto \omega^{-2/3}$.

Here, ϑ and $C(t)$ are approximated to be equal to ϑ_0 and $C_0(t)$ *i.e* the initial viscosity and the initial concentration respectively.

3. Spin coating technique

The physics of spin coating can be effectively modeled by dividing whole process into three stages : deposition and spin up, spin off and film drying. During first stage, solution is allowed to fall on a rotating substrate from a micro syringe and the substrate is accelerated to the desired speed. Spreading of the solution takes place due to centrifugal force and height is reduced to critical height.

During second stage (spin off), subsequent reduction in film height is dominated by the evaporation of the solvent. During final stage centrifugal outflow stops and further shrinkage is due to solvent loss. This results in the formation of thin film on the substrate. In actual practice these three stages overlap each other [7].

4. Experimental procedure

The spin coater consists of a variable rotating vacuum chuck powered by a motor. The slide was held firmly in position by atmospheric pressure. In a clean environment one drop 10 μml of organic Calix [4] resorcinarenes solution was allowed to fall with the help of a clean syringe onto the center of a stationary glass slide. The speed of rotation was selected to 1000 rpm and the time of rotation for 15 seconds in stage 1. The drop spreads out across the glass slide under the influence of the centrifugal force. As it moves, the solvent evaporates

form the solution leaving, a smooth continuous film of Calix [4] resorcinarenes. The spinner was brought to rest in stage 2. The same procedures were repeated with other glass slides by changing speed of rotation (2000, 3000, 4000, 5000 and 6000 rpms) keeping time of rotation same *i.e.* 15 seconds. In the second set of observations, a single drop of solution was allowed to fall onto a rotating glass slides. Similarly the speeds of rotations are changed from 1000–6000 rpm to vary the thickness of the film. Films are also prepared at different concentrations starting from 0.5 mg/ml to 5.0 mg/ml keeping speed of rotation 300 rpm and spinning time 15 seconds. All the films are studied under U 2000 spectrophotometer.

5. Film characterization

In a double beam spectrophotometer, first two bare glass slides are kept in position and the base line was measured. Then one slide is removed and the sample slide is kept. The position of the slide is adjusted such that the beam must hit the center of the film.

The spectrophotometer is connected to computer through remote control. The wavelength range selected is form 300 to 700 nm. The absorbance of the film at different wavelength is studied. The absorbance *versus* wavelength of the first set *i.e.* spun layer from rotational positions is plotted in Figure 1. As appears in the Figure 1, there is a consistence of the absorbance with respect to spin speed and peak absorbance occurs at wavelength 454 nm. The peak absorbance at 454 nm *versus* spinning speed is plotted in Figure 2, which shows the near linear relationship between them.

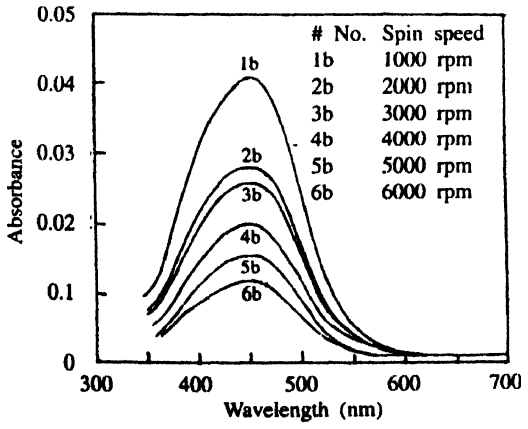

Figure 1. UV absorption spectra of spun organic film at different spinning speed.

From the absorbance film thickness is calculated taking absorbance per monolayer (ML) to be 0.0122 which has been derived from a linear dependence of absorbance

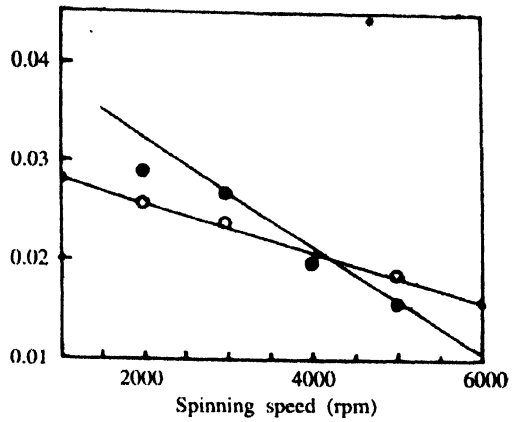

Figure 2. A plot of maximum absorbance at 454 nm as a function of spin speed : ((0) Spining from stationary : (•) spinning from motion).

versus number of monolayer obtained by Langumuir Blodgett (LB) technique. The thickness per ML is taken to be 1.6 nm as obtained from X-ray diffraction study made on LB films of the same compound [8].

The film thickness *versus* spinning speed is plotted in the Figure 3. As appears in the figure, the higher the

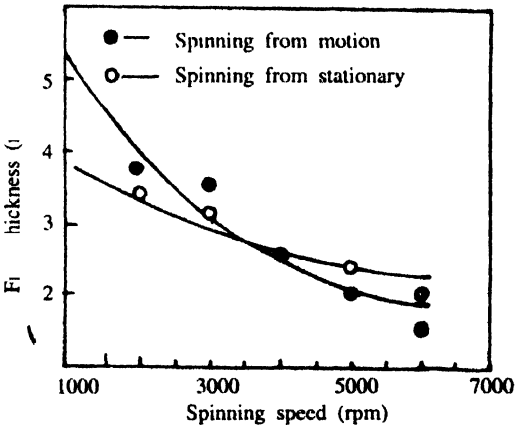

Figure 3. Film thickness as a function of spinning speed.

spinning speed the lower will be the film thickness, *i.e.* resulting films will be thinner.

Films are also prepared at different concentrations starting from 0.5 to 5.0 mg/ml at constant spinning speed of 3000 rpm and spinning time of 15 seconds. Films are studied under spectrophotometer. The absorbance *versus* wavelength is plotted in Figure 4. Consistence of absorbance with respect to concentration is also seen.

Film thickness *versus* solution concentration is plotted in Figure 5. The relation is linear.

Increasing solution concentration results in thicker film. This is because of increased fluid viscosity [9].

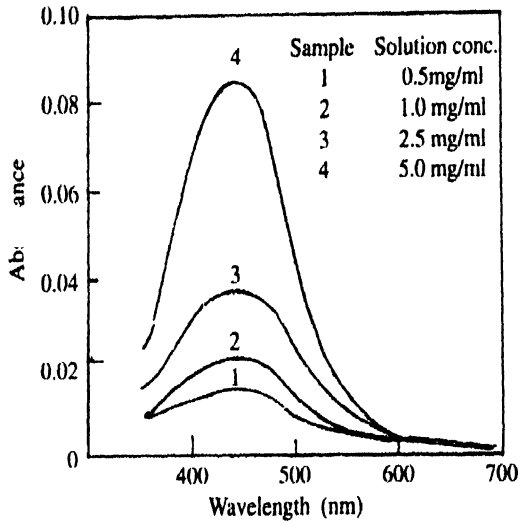

Figure 4. UV absorption spectra of spun organic film at different concentration.

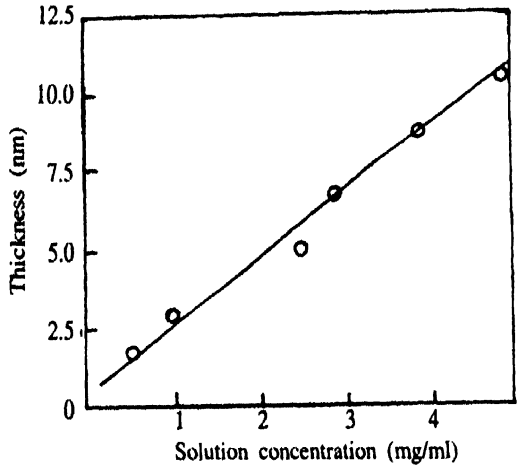

Figure 5. Film thickness as a function of solution concentration.

6. Results and discussion

Film thickness data are estimated from absorption spectra at maximum absorption and using absorption coefficient value which is derived from absorption of thin film of the same compound deposited by LB technique.

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References

[1] R Murray, P T Edwin, V Taburaza and J Olin *Semicond. Int.* **10** 172 (1987)

[2] B J J Zelinski and D R Uhlmann *J. Phys. Chem. Solids* **45** 1069 (1984)

[3] T M Parrill *J. Mater. Res.* **9** 723 (1994)

[4] T J Regh, J A Ochoa -Tapia, A Knoesen and B G Higgins *Appl Opt.* **28** 5215 (1989)

[5] A G Emsile, F T Bonner and L G Peck *J. Appl. Phys.* **29** 858 (1958)

[6] D Meyerhofer *J. Appl. Phys.* **49** 3993 (1978)

[7] R K Yonkoski and D S Soane *J. Appl. Phys.* **72** 725 (1992)

[8] O Omar, A K Ray, A K Hassan and F Davis *Supramolecular Sci* **4** 417 (1997)

[9] W W Flack, D S Soong, A T Bell and D W Hess *J. Appl. Phys.* **56** 1199 (1983)